



Project Summary

Experimental Investigation of PIC Formation in CFC-12 Incineration

Bruce Springsteen and Garth R. Hassel

Experiments were conducted to determine the effect of flame zone temperature on gas-phase flame formation and destruction of products of incomplete combustion (PICs) during dichlorodifluoromethane (CFC-12) incineration. The effect of water injection into the flame zone was also studied. Tests involved burning CFC-12 in a propane gas flame. Combustion gas samples were taken and analyzed for volatile organic compounds as well as polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/PCDF).

PCDD/PCDF were not detected at baseline operating conditions (1204°C and 9.3% CFC-12 by volume in fuel). Low levels of PCDD/PCDF were detected in the combustion gas at a lower temperature (913°C). Poor combustion conditions producing smoke and soot may have contributed to the formation of PCDD/PCDF. Low levels of PCDD/PCDF were also detected at the lower temperature with water injection into the flame zone. Flame zone water injection may have a reducing effect on PCDD/PCDF formation during CFC-12 incineration.

Halogenated PICs including chloromethane, vinyl chloride, CFC-11, dichloroethane, chloroform, trichloroethane, chlorobenzene, dichloropropene, carbon tetrachloride, methylene chloride, and tetrachloroethene were detected during CFC-12 incineration. Aromatic compounds such as benzene, toluene, and xylene were also detected. Water injection into the flame zone did not impact PIC formation. Halogenated and non-halogenated PIC

compounds and levels were influenced by flame zone temperature and combustion efficiency; higher temperature and lower carbon monoxide (CO) and total unburned hydrocarbon (THC) flue gas concentrations resulted in lower PIC levels. CFC-12 destruction efficiencies (DE) of 99.98% were obtained. DEs were independent of flame zone temperature, stoichiometric ration, or CO and THC flue gas concentrations.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A bench scale test program was conducted in 1991 by Energy and Environmental Research Corporation (EER) to characterize combustion emissions from chlorofluorocarbon (CFC) incineration. CFC destruction efficiencies of 99.999% were obtained. Chlorinated and aromatic products of incomplete combustion (PICs) were identified in the flue gas. Significant levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) were also detected. The high levels of PCDD/PCDF contrast results from CFC incineration pilot scale tests conducted recently by T-Thermal. Preliminary results from T-Thermal show PCDD/PCDF found at moderate levels in tests with high input of CFC and were not present in tests with low CFC input. The T-Thermal tests were per-

formed at higher temperature (1093°F) and with water injection into the combustion zone. The higher temperature and/or water injection were considered as possible reasons for the difference in PCDD/PCDF formation measured for these two programs.

The strong effects of lowering the emissions of chlorinated PICs (chlorobenzenes in particular) by water injection have recently been demonstrated in a study of thermal destruction of CFCs. Other results reported recently by the fundamental studies of thermal destruction of chlorohydrocarbons suggest that PIC formation during the incineration of high chlorine content organics, such as CFCs, occurs through complex reactions. Such reactions will likely occur in the oxygen-

deficient regions of the incineration flame zone created by incomplete mixing.

Thermal incineration is the only technology available at a commercial scale for CFC destruction. Therefore, it is desirable to evaluate the risks associated with its use. Because no significant CFC incineration test burn data are available, this test program provides further information on the formation of PICs and their control during CFC incineration. Specifically, this program investigated:

- Effects of incineration flame zone temperature on the combustion gas characteristics (in particular the range of temperatures which lead to gas-phase formation of PCDD/PCDF) in order to determine the relation between com-

bustion gas characteristics and combustion conditions, and

- Effects of supplying additional (OH) into the flame zone through water injection on PIC and PCDD/PCDF formation.

Experimental

EER's Controlled Temperature Tower (CTT) furnace was used for this study. The furnace is shown in Figure 1. This pilot scale facility has an inside diameter (ID) of 8 in.* and an overall furnace length of 94 in. The reactor entry consists of an 18 in. long quarl that diverges from 2 in. at the burner to the full 8 in. ID.

The test matrix is shown in Table 1. Test 1 involved firing only propane fuel to evaluate the background organic species that are attributable to the fuel and system. The rest of the tests involved mixing dichlorodifluoromethane (CFC-12) directly with propane upstream of the burner gun. Test 2 was performed with a mixture of 9.3% CFC-12 and 90.7% propane fuel by volume at the same baseline temperature as Test 1. The temperature of Test 3 was based on PCDD/PCDF results from Test 2. If PCDD/PCDF levels were considered to be significantly high, Test 3 would have been performed at a higher temperature than baseline; however, because levels were low, Test 3 was performed at a lower temperature. Test 4 was performed at the same temperature as Test 3 with the addition of water injection into the flame zone to determine the potential PIC and PCDD/PCDF formation reduction effect.

Flue gas temperatures were measured at the four different furnace locations, shown in Figure 1. Temperatures were measured with K-type thermocouples (TC). Also, pre- and post-test temperatures were measured using a suction pyrometer containing a B-type TC to get more accurate high temperature readings.

Flue gas was sampled for volatile organics using EPA SW 846 Method 0030 and PCDD/PCDF using EPA Method 23 during each test. Also, the flue gas was monitored for combustion products (O₂, CO₂, CO, NO, and THC) using a continuous emissions monitoring system (CEMS). The sampling locations are shown in Figure 1.

Results

Individual test conditions, including CFC-12/fuel injection rate, water injection rate, furnace firing rate, flame stoichiometry, flue gas composition (O₂, CO₂, NO, CO,

* 1 in. = 2.54 cm.

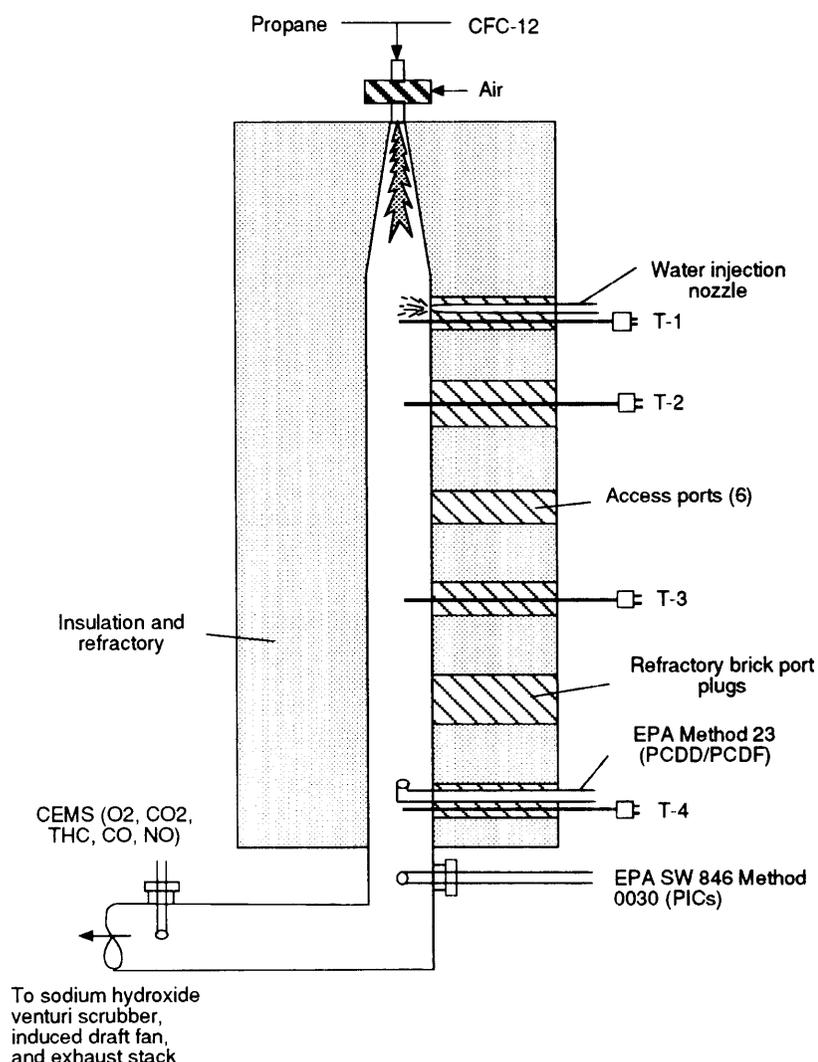


Figure 1. Experimental controlled temperature tower (CTT) facility

Table 1. Test Matrix

Test No.	CFC-12/fuel ratio (volume %)	Temperature	Water injection
1	0	baseline	no
2	9.3	baseline	no
3	10.0	high or low ^a	no
4	10.0	high or low ^a	yes

^a Chosen temperature depends on PCDD/PCDF results from Test 2

THC, and moisture content), and flue gas temperature, are summarized in Table 2.

PCDD/PCDF flue gas levels are given in Table 3, both as flue gas concentration and generation rate based on CFC-12 burning rate. PCDD/PCDF were not detected in Test 1 (system blank) or Test 2 (baseline condition of 1204°C with 9.3% CFC-12 by volume in fuel).

Low concentrations of octa-CDD (6.2 ng/dscm) and octa-CDF (97 ng/dscm) were detected during Test 3. Poor combustion conditions were present during Test 3. Flame smoking and sooting was present due to reduced excess oxygen, low temperature, and apparently insufficient fuel/air mixing; a layer of fine black particulate (soot) was observed in the flue gas sampling train equipment. High concentrations of CO (270 ppmv) and THC (540 ppmv) were present in the flue gas.

Low concentrations of hepta-CDF (6.7 ng/dscm) and octa-CDF (14 ng/dscm) were detected in Test 4 which was performed with water injection into the flame zone. Sampling train filters and lines were clean; no particulate buildup or discoloration of the sampling equipment was observed. High levels of CO (670 ppmv) and THC (650 ppmv) were present.

PICs are given in Table 4. Many chlorinated PICs were detected at the baseline conditions (Test 2), including chlorinated hydrocarbons (CHCs) such as chloromethane, dichloroethane, methylene

chloride, chloroform, and carbon tetrachloride. CFC-11 was also detected. Non-halogenated aromatics including toluene, xylene, and benzene were also present.

More species and higher concentrations of chlorinated PICs were detected during Tests 3 and 4 compared with the baseline Test 2. PICs formed during the lower temperature Tests 3 and 4 included those detected during the baseline Test 2; also, CHCs such as chloroethane, vinyl chloride, trichloroethane, tetrachloroethene, dichloropropene, and chlorobenzene were identified. Higher levels of benzene were detected in the lower-temperature Tests 3 and 4.

Tentatively identified compounds (TICs) identified from the EPA SW 846 Method 0030 sampling train are given in Table 5. Relatively high levels of dichlorodifluoromethane (CFC-12) were detected in the flue gas during all three tests which involved CFC-12 incineration. CFC-12 DEs of 99.982, 99.985, and 99.980% were observed for Tests 2, 3, and 4, respectively. Other halogenated TICs that were identified in Tests 3 and 4 include difluorodimethylsilane, fluorotrimethylsilane, and chloropropene.

Conclusions

PCDD/PCDF were not detected at furnace baseline temperature and operating conditions (1204°C, 15.8 kW, and 9.3% CFC-12 by volume in fuel). At these CFC-

12 incineration conditions, there is no tendency for PCDD/PCDF to form within the primary flame. PCDD/PCDF levels detected by another study during CFC-12 incineration were very likely due to catalytic formation in the metal exhaust duct in the presence of copper at a flue gas temperature range of 149-371°C.

Low levels of PCDD/PCDF were detected at lower temperature operating conditions (954°C, 9.38 kW). Poor combustion conditions producing smoke and soot may have contributed to the formation of PCDD/PCDF. Low levels of PCDD/PCDF were also detected at lower temperatures with water injection into the flame zone. PCDD/PCDF formation may be attributable to homogeneous flame gas-phase reactions or heterogeneous reactions between precursors on soot and fine particulate matter. Water injection reduced PCDD/PCDF levels by a factor of 5; however poor combustion conditions during the test without water may have been responsible for the higher levels of PCDD/PCDF.

Halogenated PICs such as chloromethane, vinyl chloride, CFC-11, dichloroethane, chloroform, trichloroethane, carbon tetrachloride, and tetrachloroethene were observed during CFC-12 incineration. Water injection into the flame zone did not have an effect on volatile PIC formation. Halogenated and non-halogenated PIC species and concentration levels were influenced by flame conditions; higher temperature and lower CO and THC flue gas concentrations resulted in formation of a fewer number of PIC species at lower concentrations. CFC-12 DEs of 99.98% were obtained. DEs were independent of flame zone temperature, stoichiometric ratio, or CO and THC flue gas concentrations.

Table 2. Summary of Test Conditions

Test No.	Primary flame					Flue gas composition						Flue gas temperature			
	CFC-12 in fuel		Water injection g/min	Firing rate MM Btu/hr ^a	SR ^b	O ₂	CO ₂	CO	NO	THC	H ₂ O	T-1	T-2	T-3	T-4
	vol	wt				dry	dry	dry	dry	dry	wet				
	%	%		ppmv ^c	ppmv ^c	ppmv ^c	ppmv ^c	ppmv ^c	vol %	°F ^d	°F	°F	°F		
1	0.0	0.0	0	0.054	1.4	6.1	7.6	58	66	11	6.0	2200	1850	1500	1200
2	9.3	22.0	0	0.054	1.4	6.1	7.2	56	63	12	8.4	2130	1700	1430	1130
3	10.0	23.4	0	0.032	1.1	2.0	6.6	267	30	540	3.5	1675	1086	860	716
4	10.0	23.4	40	0.032	1.7	9.4	6.1	671	29	650	7.1	1400	1040	795	660

^a Btu/hr = 0.293 W.

^b Stoichiometric ratio.

^c @ 7% O₂.

^d °C = 5/9 (°F-32).

Table 3. Summary of PCDD/PCDF Flue Gas Levels

Species	Flue gas concentration (ng/dscm) ^a				Generation rate (ng/g of CFC-12)			
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4
PCDD								
TCDD	nd ^b	nd	nd	nd	n/a ^c	nd	nd	nd
PeCDD	nd	nd	nd	nd	n/a	nd	nd	nd
HxCDD	nd	nd	nd	nd	n/a	nd	nd	nd
HpCDD	nd	nd	nd	nd	n/a	nd	nd	nd
OCDD	nd	nd	6.2	nd	n/a	nd	0.47	nd
Total PCDD	nd	nd	6.2	nd	n/a	nd	0.47	nd
PCDF								
TCDF	nd	nd	nd	nd	n/a	nd	nd	nd
PeCDF	nd	nd	nd	nd	n/a	nd	nd	nd
HxCDF	nd	nd	nd	nd	n/a	nd	nd	nd
HpCDF	nd	nd	nd	6.7	n/a	nd	nd	0.5
OCDF	nd	nd	97	14	n/a	nd	7.4	1.1
Total PCDF	nd	nd	97	21	n/a	nd	7.4	1.6
Total PCDD/PCDF	nd	nd	103	21	n/a	nd	7.9	1.6

^a @ 7% O₂.

^b Not detected in sample (below method detection limit).

^c Not appropriate.

Table 4. Summary of PIC Flue Gas Levels^a

Compound	Flue Gas Concentration (µg/dscm) ^b				Generation Rate (µg/g of CFC-12)			
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4
Chloromethane	150	1600	1700	1100	n/a ^d	122	130	85
Vinyl Chloride	nd ^c	nd	234	170	n/a	nd	1.8	13
Bromomethane	2.6	8	4.4	1.5	n/a	0.6	0.3	0.1
Chloroethane	nd	nd	5.5	4.2	n/a	nd	0.4	0.32
Trichlorofluoromethane	51	130	4.1	6.8	n/a	9.5	0.3	0.53
1,1-Dichloroethene	0.8	2.3	5	8.7	n/a	0.2	0.4	0.7
Acetone	18	8.4	50	9.2	n/a	0.6	3.8	0.7
Methylene Chloride	110	78	130	15	n/a	6	9.9	8.9
Trans-1,2-Dichloroethene	nd	nd	nd	nd	n/a	nd	nd	nd
1,1-Dichloroethane	nd	nd	nd	nd	n/a	nd	nd	nd
Chloroform	nd	6.5	14	10.5	n/a	0.5	1.1	0.81
1,1,1-Trichloroethane	1.3	nd	2.2	1.8	n/a	nd	0.2	0.14
Carbon Tetrachloride	nd	5.6	7.9	8.5	n/a	0.4	0.6	0.65
Benzene	15	13	650	580	n/a	0.9	49	45
1,2-Dichloroethane	nd	nd	nd	nd	n/a	nd	nd	nd
Trichloroethene	nd	nd	nd	nd	n/a	nd	nd	nd
1,2-Dichloropropane	nd	nd	nd	nd	n/a	nd	nd	nd
Bromodichloromethane	nd	nd	nd	nd	n/a	nd	nd	nd
Cis-1,3-Dichloropropene	nd	nd	1.4	6.6	n/a	nd	0.1	0.5
Toluene	20	16	49	27	n/a	1.2	3.7	2
Trans-1,3-Dichloropropene	nd	nd	0.87	1.9	n/a	nd	0.07	0.15
1,1,2-Trichloroethane	nd	nd	nd	nd	n/a	nd	nd	nd
Tetrachloroethene	nd	nd	2.5	4.4	n/a	nd	0.2	0.34
Dibromochloromethane	nd	nd	nd	0.72	n/a	nd	nd	0.06
Chlorobenzene	nd	nd	2.8	2.7	n/a	nd	0.2	0.2
Ethyl Benzene	nd	nd	0.82	0.81	n/a	nd	0.06	0.06
M,P-Xylene	4.15	1.7	2	2.1	n/a	0.1	0.15	0.16
O-Xylene	nd	nd	0.7	0.34	n/a	nd	0.05	0.03

Table 4. Summary of PIC Flue Gas Levels * (continued)

Compound	Flue Gas Concentration ($\mu\text{g}/\text{dscm}$) ^b				Generation Rate ($\mu\text{g}/\text{g}$ of CFC-12)			
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4
Bromoform	nd	nd	nd	nd	n/a	nd	nd	nd
1,1,2,2-Tetrachloroethane	nd	nd	nd	nd	n/a	nd	nd	nd
1,2-Dichlorobenzene	nd	nd	nd	nd	n/a	nd	nd	nd
1,4-Dichlorobenzene	nd	nd	nd	nd	n/a	nd	nd	nd
1,3-Dichlorobenzene	nd	nd	nd	nd	n/a	nd	nd	nd

* From SW 486 Method 0030 flue gas sampling train and SW 846 8240 Analytical Method.

^b @ 7% O₂.

^c Not detected in sample (below Method detection limit).

^d Not appropriate.

Table 5. Summary of TIC Flue Gas Levels *

Compound	Flue Gas Concentration ($\mu\text{g}/\text{dscm}$) ^b				Generation Rate ($\mu\text{g}/\text{g}$ of CFC-12)			
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4
Dichlorodifluoromethane		2400	1900	2600	n/a ^c	180	150	200
Difluorodimethylsilane	78	798	10		n/a	60	0.8	
Methylpropane	12				n/a			
Sulfur Dioxide			4.6	12	n/a		0.4	0.9
Methanethiol	33	98		41	n/a	74		3.1
Fluorotrimethylsilane		430	15	51	n/a	32	1.1	3.9
Dichloroethyl Ether	26	28			n/a	2.1		
Chlorotrimethylsilane		57			n/a	4.3		
Thiobismethane	22	9		18	n/a	0.7		1.4
Chloropropene			21	53	n/a		1.6	4.1
Methoxytrimethylsilane		11			n/a	0.8		
Hexane	24				n/a			
Dihydrofuran	3.3				n/a			
Methylfuran	7.3				n/a			
Nitromethane				1	n/a			0.07
Ethylbenzene	1.9				n/a			
Methylethylbenzene	4.8				n/a			
Trifluoro Ester		3.9			n/a	0.3		
Naphthalene			26	10	n/a		2	0.8

* From SW 846 Method 0030 flue gas sampling train.

^b @ 7% O₂.

^c Not appropriate.

B. Springsteen and G.R. Hassel are with Energy and Environmental Research Corp., Santa Ana, CA 92705.

C.W. Lee is the EPA Project Officer (see below).

The complete report, entitled "Experimental Investigation of PIC Formation in CFC-12 Incineration," (Order No. PB93-191294/AS; Cost: \$27.00, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Project Officer can be contacted at:

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